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TITLE: Photosensitive recording material for transparent hologram prepd. using solvent-soluble resin and radical photoinitiators and sensitising dye

INVENTOR: ITO H; OE Y

PATENT-ASSIGNEE: TOPPAN PRINTING CO LTD[TOPP]

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ABSTRACTED-PUB-NO: JP 08190334 A

BASIC-ABSTRACT:

Photosensitive recording material for transparent hologram mfr. by forming a coherent pattern by projecting reference light which is coherent chemical action radiation and object light which is the same radiation to a recording

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medium comprises: (A) resin which is solvent soluble and solid at normal temp. and normal pressure; (B) polymerising monomer which has at least one radical polymerisable ethylene unsatd. bonding which is liq. at normal temp. and normal pressure and which has b.pt. of 100°C at normal pressure and has different refractive index with the component (A); (C) photo initiator for activating radical polymerisation when it is exposed by chemical action; (D) sensitising dye having amino gp. for sensitising the photo initiator (C); and (E) cpd. for generating sulphonic acid deriv. by action such as light or heat.

USE - The material is used for hologram optical element such as head-up display.

ADVANTAGE - The material has high transparency in a visible light in dry processing and also improved heat resistance and the hologram is chemically stable. In particular, the material is used for photosensitive recording material for transparent hologram for the hologram optical element (HOE) such as the head up display.

TITLE-TERMS: PHOTSENSITISER RECORD MATERIAL TRANSPARENT HOLOGRAM PREPARATION
SOLVENT SOLUBLE RESIN RADICAL POLYMERISE ETHYLENE
MONOMER PHOTOINITIATOR SENSITIVE DYE

DERWENT-CLASS: A89 G06 P84 V07 W04

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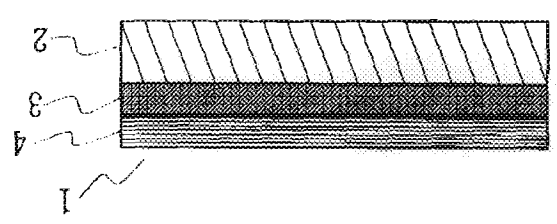
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(71) 出願人 000033193 凸版印刷株式会社
東京都台東区台東 1 丁目 5 番 1 号
(72) 発明者 伊藤 浩光
東京都台東区台東 1 丁目 5 番 1 号 凸版印刷株式会社内
(72) 発明者 大江 靖
東京都台東区台東 1 丁目 5 番 1 号 凸版印刷株式会社内

(54) [発明の名称] 透明ホログラム用感光性記録媒体並びにそれを用いた透明ホログラムの製造方法

(57) [要約]
【目的】乾式処理によるホログラム形成が可能であり、高透明性であるとともに耐候性に優れ、かつ高解像度、高回折効率、再生波長再現性に優れた透明ホログラムを提供する。
【構成】(A) 溶媒可溶性で常温、常圧で固体である樹脂と、(B) 常温、常圧で液体で、かつ常圧で沸点が100℃以上であるラジカル重合可能なエチレン性不飽和結合を少なくとも1個以上有し、かつ(A)と屈折率の異なる重合性モノマーと、(C) 露光するとラジカル重合を活性化する光開始剤と、アミノ基を有する増感色素と、(E) 光或いは熱などの外的作用によりスルホン酸誘導体を生成する化合物から構成され、(E) 化合物から生成されるスルホン酸誘導体により、記録媒体中に残留する増感色素がスルホン酸誘導体によって退色する。

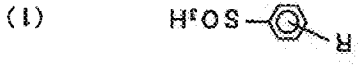


【特許請求の範囲】

【請求項1】記録媒体中にコヒーレントな化学作用放射線である参照光と、同じ放射線である対象光とを入射して干渉パターンを形成しホログラムを作成する透明ホログラム用感光性記録材料において、本質的に、(A) 溶媒可溶性で常温、常圧で固体である樹脂と、(B) 常温、常圧で液体で、かつ常圧で沸点が100℃以上であるラジカル重合可能なエチレン性不飽和結合を少なくとも1個以上有し、かつ成分(A)と屈折率の異なる重合性モノマーと、(C) 化学作用放射線に露光するとラジカル重合を活性化化する光開始剤と、(D) 光開始剤

(C)を増感するアミノ基を有する増感色素と、(E) 光あるいは熱などの外的作用によりスルホン酸誘導体を生成する化合物からなることを特徴とする透明ホログラム用感光性記録材料。

【請求項2】光あるいは熱などの外的作用により生成するスルホン酸誘導体が下記一般式(1)で表されることを特徴とする請求項1記載の透明ホログラム用感光性記録材料。



【化1】

録材料。

を特徴とする請求項1記載の透明ホログラム用感光性記録材料。

【請求項3】請求項1記載の透明ホログラム用感光性記録材料を溶解して調製した感光液を基板上に塗布、乾燥してなる感光層と、保護層とを設けてなることを特徴とする透明ホログラム用感光性記録媒体。

【請求項4】請求項3記載の透明ホログラム用感光性記録媒体の感光層に対して、ホログラフィックな露光を施し潜像を形成した後、光あるいは熱などの外的作用を与え、前記スルホン酸誘導体を生成する化合物から生成されるスルホン酸誘導体により前記アミノ基を有する増感色素を退色又は消色してなることを特徴とする透明ホログラムの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、体積位相型ホログラム形成に用いられ、可視光、とくにアルゴブルーザ光などの可視光に高感度で感光し、かつ解像度、回折効率、透明性などのホログラム特性値が良好であり、さらに耐候性及び保存安定性に優れた透明ホログラム用感光性記録材料及び透明ホログラム用感光性記録媒体並びにそれを用いた透明ホログラムの製造方法に関する。

【0002】

【従来の技術】従来、ホログラムは三次元立体像の再生が可能であることから、その優れた意匠性、装飾効果から書籍、雑誌等の表紙、POPなどのディスプレイ、キ

フトなどに利用されている。またホログラムはサミツロン単位での情報の記録と等価であるといえることから有価証券、クレジットカードなどの偽造防止用のマークなどにも利用されている。

【0003】とくに体積位相型ホログラムは、ホログラム記録媒体中に光学的吸収ではなく屈折率の異なる空間的な干渉縞を形成することによって、像を通過する光ビームを吸収することなく位相を変動することができ、ため、近年においては、ディスプレイ用途の他に、自動車搭載用のヘッドアップディスプレイ(HUD)に代表されるホログラム光学素子(HOE)への応用が期待されている。

【0004】ところで体積位相型ホログラム記録材料は、可視発振波長を持つレーザ光に高感度で感光し、しかも高い解像性を示すことが要求されている。また、実際にホログラムの形成に使用するに当たり、ホログラムの回折効率、再生光の波長再現性やパンド幅(再生光ビームの半値幅)等の特性がその目的に合うことが要求される。とくにヘッドアップディスプレイ(HUD)など

の使用される場合には上記ホログラム特性だけでなく、より高い透明性(光透過性)を有することが重要視されている。さらに、長期にわたって保存安定性に優れていることも必要とされている。

【0005】ホログラム作製に関する一般の原理は、いくつかの文献や専門書、たとえば「ホログラフィックイマジン」(江内順平編;産業図書)2章に記載されている。これらによれば、二光束のコヒーレントな一般には、レーザ光の一方を記録対象物に照射し、それからその全反射光を受け取れる位置に感光性の記録媒体、例えば写真用乾板が置かれる。記録媒体には、対象物からの反射光の他に、もう一方のコヒーレントな光が、対象物に当たらずに直接照射される。対象物からの反射光を対

象光、また直接媒体に照射される光を参照光といい、参照光と対象光との干渉縞が画像情報として記録される。次に、処理された記録媒体が光に曝され、適切な位置で観測されると、照明光源からの光は、記録の際に設置された記録媒体に最初に到達した反射光の液面を再現するようにホログラムによって回折され、その結果、対象物の実像と似た物体像が三次元的に観測される。参照光と対象光を同じ方向から記録媒体に入射させて形成されるホログラムは透過型ホログラムとして知られてい

る。一方、互いに記録媒体の反対側から入射させて形成したホログラムは、一般に反射型ホログラムとして知られている。透過型ホログラムは、例えば米国特許第3506327号公報、米国特許第3894787号公報などによって開示されているような公知の方法によって得ることができる。また、反射型ホログラムは、例えば米国特許第3532406号公報に開示された公知の方法で作製

【0006】像として形成されたホログラムを比較することができる。

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(4)

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射により、定着される。

【0012】また米国特許第3658526号公報に開

示されたホログラム記録材料の製造法も含めた改良技術

として、米国特許第4942112号公報および米国特

許第5098803号公報、また特開平2-3081号

公報および特開平2-3082号公報に開示されてい

る。これらには熱可塑性樹脂、重合可能な不飽和エチレ

ン性モノマーおよび光重合開始剤を基本組成とし、屈折

率変調を向上させるために熱可塑性樹脂または重合可能

な不飽和エチレン性モノマーのどちらか一方に芳香環を

有する化合物を用いて屈折率差となるようにし、また米

国特許第3658526号公報に開示されているものと同

様に、高分子量の樹脂をバリエーションとして

使用することによる露光時のモノマーの拡散性の制限か

ら、多くの露光量が必要となると共に高い屈折率を得

ることができないため、非反応性の可塑性剤を添加してい

る。

【0013】また特開平5-107999号公報によれ

ば、上記特許における可塑性剤の代わりにカチオン重合性

モノマーおよびカチオン重合開始剤を配合したものが提

案されている。さらに、エポキシ樹脂とラジカル重合性

不飽和エチレン性モノマーおよびラジカル重合剤から

なるホログラム記録用感光性樹脂組成物が特開平5-9

4014に開示されている。

【0014】

【発明が解決しようとする課題】上記した体積位相型ホ

ログラムの記録材料は、屈折率変調を得るためのモノマ

ーの重合性あるいは分散性の問題、またモノマーを担持す

る担体及び非反応性添加剤の添加による保存安定性の問

題等や、さらにはホログラム作製における作業性、得ら

れるホログラムの屈折率、透明性、再現性などのホロ

グラム特性の問題をそれぞれ有しているが、とくに乾式

現像法を用いる光重合型感光材料においては、全てに共通

した課題としてホログラム形成時に使用された増感色素

が、そのまま系内に残留するため、着色したホログラム

となる問題があり、とくに高い透過率が要求されるヘッ

ドアップディスプレイ(HUD)など光学素子の用途に

おいては、深刻な問題となっている。そこで本発明は乾

式処理によるホログラム形成が可能であり、高透明性で

あるとともに耐候性に優れ、かつ高解像度、高屈折効

率、再生波長再現性に優れた透明ホログラム感光性記録

材料及び透明ホログラム感光性記録媒体並びにそれを用

いた透明ホログラムの製造方法を提供することを目的と

する。

【0015】

【課題を解決するための手段】本発明は上記課題を解決

すべくなされたものであり、請求項1記載の発明は、記

録媒体中にコヒーレントな化学作用放射線である参照光

と、同じ放射線である対象光とを入射して干渉パターン

を形成しホログラムを作成する透明ホログラム用感光性

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記録材料において、本質的に、(A)溶解可溶性で常

温、常圧で固体である樹脂と、(B)常温、常圧で液体

で、かつ常圧で沸点が100℃以上であるラジカル重合

可能なエチレン性不飽和結合を少なくとも1個以上有

し、かつ成分(A)と屈折率の異なる重合性モノマ

ーと、(C)化学作用放射線に露光するとラジカル重合を

活性化する光開始剤と、(D)光開始剤(C)を増感す

るアミノ基を有する増感色素と、(E)光あるいは熱な

どの外的作用によりアルホノ酸誘導体を生ずる化合物

からなることを特徴とする透明ホログラム用感光性記録

材料である。

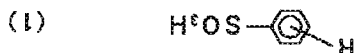
【0016】請求項2記載の発明は、請求項1の透明ホ

ログラム用感光性記録材料において、アルホノ酸誘導体

を生ずる化合物が下記一般式(1)で表されることを

特徴とする。

【化2】



(式中、Rは水素原子、アルキル基、ハロゲン基、ニト

ロ基、ヒドロキシ基、シアノ基、アミノ基あるいはアル

コキシ基からなる一つ以上の置換基で芳香環を置換して

なることを示す。)

【0017】請求項3記載の発明は、請求項1記載の透

明ホログラム用感光性記録材料を溶媒に溶解して調製し

た感光液を基板上に塗布、乾燥してなる感光層と、保護

層とを設けてなることを特徴とする透明ホログラム用感

光性記録媒体である。

【0018】請求項4記載の発明は、請求項3記載の透

明ホログラム用感光性記録媒体の感光層に対して、ホロ

グラフィックな露光を施し潜像を形成した後、光あるい

は熱などの外的作用を与え、前記アルホノ酸誘導体を生

成する化合物から生成されるアルホノ酸誘導体により前

記アミノ基を有する増感色素を退色又は消色してなるこ

とを特徴とする透明ホログラムの製造方法である。

【0019】

【作用】本発明によれば、ラジカル重合可能な脂肪族モ

ノマー(B)は、溶解可溶性で常温、常圧で固体である

樹脂(A)に均一に分布しているが、この記録材料にし

てラジ干渉光を照射することにより、レーザー照射部位中の

光干渉作用の強い部位において、光開始剤(D)が増感

色素(C)の作用で光開始剤(D)から生じたラジカル

重合活性種により、脂肪族モノマー(B)が重合しポリ

マー化するに伴い、その濃度差が生じるため、周囲から

脂肪族モノマー(B)が拡散移動する。すなわちレーザー

照射部位中の光干渉作用の強い部位においてはモノマ

ー濃度が高くなり、レーザー照射部位中の光干渉作用の強い

部位においては低くなる。また、樹脂(A)はレーザー照

射部位中の光干渉作用の弱い部位に押し出され、その部

分の濃度が高くなり、レーザー照射部位中光干渉

作用の強い部位での濃度は低下する。これにより、両部

ニカムのフロリド、フロミド、あるいはホウケツ化塩、
ハギサルオロフスエート塩、ハギサルオロアル
セネード塩等のヨードニウム塩、トリアリールアルホニ
ウム塩、トリアリールホスニウム塩、さらに繁アレー
ン錯体などの他に、tertiaryアルキルオキシドー

so-ツタル、2, 5-シキナル-2, 5-エヌ
(ハソツタルシキ) ハサソ、1, 4-エヌ[α-
(tert-ツタルシキ) -iso-プロホキシ]
メセソ、シ-tert-ツタルシキ、2, 5
-シキナル-2, 5-エヌ(tert-ツタルシキ)

(イ) ヲキセシユセフヨルオキシド、 α -（150-70℃）ニル）-iso-70℃ニルオキシ
 F、2、5-エタ（レフロノキシ）-2、5-ジメチルヘキサ、tert-ブチルクロロキシド、
 I、1-エタ（tert-ブチルオキシ）-3、3、

3, 3', 4, 4' - フトリ (tert-butyl) エチルベンゼン
 3, 3', 4, 4' - フトリ (tert-butyl) エチルベンゼン
 3, 3', 4, 4' - フトリ (tert-butyl) エチルベンゼン

[illegible]

ert-アルルオキシベンゾエト、ジ-tert
 -アルルオキシイソブチレートなどの有機過酸化
 物や、9, 10-アノキノン、1-クロロアノ
 キノン、2-クロロアノキノン、オクタフル
 スオキシ、1, 2-ビスアノキソンのキノ

ノ類や、ペンノインメチル、ペンノインエチルエーテル、 α -メチルペンノイン、 α -ブチルペンノインなどのペンノイン誘導体等を挙げることができる。

【0027】さらに、本発明の光増感剤(C)を増感する1種類以上のアミノ基を有する成分(D)増感色素と

しては、具体的にはロータミンB、クリスタルバイオレ
 ット、マカイトグリーン、オーミンO、ホスファソ
 ン、アクリルモノレジン、アクリルメタクリレート、セト
 ラセンT、アクリルメタクリルアルコール、ニユートラ
 ルレック、チオニソ、メチレンブルー、イソジヤ、ピナ

シフール、フトラフエニホリナリシ、3、3' -
カルニルニエヌ(7-ジエナルニカニシ、3-
(2'-スニフナール)-7-ジエナルニカニシ、3-
リシ、3-(2'-スニフナール)-7-ジエナルニカニシ、3、3' -
ルニミナカニシ、3、3' -カルニルニエヌ(7-ジ

[illegible]

フル-7-ジエフルミノカクリン、7-ジエフルミ
 ノ-3-(4-ヨ-Fスゾイル)クアリシ、7-ジエ
 フルミノ-3-(4-ジエフルミノスゾイル)ク
 アリシ、2-スゾイル-3-(p-ジエフルミノ
 エニル)-2-7口スゾニトリル、2,5-EA [14]

[illegible]

E742=U/L/F/H/V/N {V/F} X (F/U)/K- (H
I) Z-V/F-E-I) } -Z-V/F-E-E } E
A42=U/L/F/H/V/N-H E {V/F} X (F/U)/N/L
P/H/V/N-Z-V/F-E-E) } -Z-V/F-E-E } S
(F) V/O/Z-E {S/G} X (F)/N-F-E-N/M/F


1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100. 101. 102. 103. 104. 105. 106. 107. 108. 109. 110. 111. 112. 113. 114. 115. 116. 117. 118. 119. 120. 121. 122. 123. 124. 125. 126. 127. 128. 129. 130. 131. 132. 133. 134. 135. 136. 137. 138. 139. 140. 141. 142. 143. 144. 145. 146. 147. 148. 149. 150. 151. 152. 153. 154. 155. 156. 157. 158. 159. 160. 161. 162. 163. 164. 165. 166. 167. 168. 169. 170. 171. 172. 173. 174. 175. 176. 177. 178. 179. 180. 181. 182. 183. 184. 185. 186. 187. 188. 189. 190. 191. 192. 193. 194. 195. 196. 197. 198. 199. 200. 201. 202. 203. 204. 205. 206. 207. 208. 209. 210. 211. 212. 213. 214. 215. 216. 217. 218. 219. 220. 221. 222. 223. 224. 225. 226. 227. 228. 229. 230. 231. 232. 233. 234. 235. 236. 237. 238. 239. 240. 241. 242. 243. 244. 245. 246. 247. 248. 249. 250. 251. 252. 253. 254. 255. 256. 257. 258. 259. 260. 261. 262. 263. 264. 265. 266. 267. 268. 269. 270. 271. 272. 273. 274. 275. 276. 277. 278. 279. 280. 281. 282. 283. 284. 285. 286. 287. 288. 289. 290. 291. 292. 293. 294. 295. 296. 297. 298. 299. 300. 301. 302. 303. 304. 305. 306. 307. 308. 309. 310. 311. 312. 313. 314. 315. 316. 317. 318. 319. 320. 321. 322. 323. 324. 325. 326. 327. 328. 329. 330. 331. 332. 333. 334. 335. 336. 337. 338. 339. 340. 341. 342. 343. 344. 345. 346. 347. 348. 349. 350. 351. 352. 353. 354. 355. 356. 357. 358. 359. 360. 361. 362. 363. 364. 365. 366. 367. 368. 369. 370. 371. 372. 373. 374. 375. 376. 377. 378. 379. 380. 381. 382. 383. 384. 385. 386. 387. 388. 389. 390. 391. 392. 393. 394. 395. 396. 397. 398. 399. 400. 401. 402. 403. 404. 405. 406. 407. 408. 409. 410. 411. 412. 413. 414. 415. 416. 417. 418. 419. 420. 421. 422. 423. 424. 425. 426. 427. 428. 429. 430. 431. 432. 433. 434. 435. 436. 437. 438. 439. 440. 441. 442. 443. 444. 445. 446. 447. 448. 449. 450. 451. 452. 453. 454. 455. 456. 457. 458. 459. 460. 461. 462. 463. 464. 465. 466. 467. 468. 469. 470. 471. 472. 473. 474. 475. 476. 477. 478. 479. 480. 481. 482. 483. 484. 485. 486. 487. 488. 489. 490. 491. 492. 493. 494. 495. 496. 497. 498. 499. 500. 501. 502. 503. 504. 505. 506. 507. 508. 509. 510. 511. 512. 513. 514. 515. 516. 517. 518. 519. 520. 521. 522. 523. 524. 525. 526. 527. 528. 529. 530. 531. 532. 533. 534. 535. 536. 537. 538. 539. 540. 541. 542. 543. 544. 545. 546. 547. 548. 549. 550. 551. 552. 553. 554. 555. 556. 557. 558. 559. 560. 561. 562. 563. 564. 565. 566. 567. 568. 569. 570. 571. 572. 573. 574. 575. 576. 577. 578. 579. 580. 581. 582. 583. 584. 585. 586. 587. 588. 589. 590. 591. 592. 593. 594. 595. 596. 597. 598. 599. 600. 601. 602. 603. 604. 605. 606. 607. 608. 609. 610. 611. 612. 613. 614. 615. 616. 617. 618. 619. 620. 621. 622. 623. 624. 625. 626. 627. 628. 629. 630. 631. 632. 633. 634. 635. 636. 637. 638. 639. 640. 641. 642. 643. 644. 645. 646. 647. 648. 649. 650. 651. 652. 653. 654. 655. 656. 657. 658. 659. 660. 661. 662. 663. 664. 665. 666. 667. 668. 669. 670. 671. 672. 673. 674. 675. 676. 677. 678. 679. 680. 681. 682. 683. 684. 685. 686. 687. 688. 689. 690. 691. 692. 693. 694. 695. 696. 697. 698. 699. 700. 701. 702. 703. 704. 705. 706. 707. 708. 709. 710. 711. 712. 713. 714. 715. 716. 717. 718. 719. 720. 721. 722. 723. 724. 725. 726. 727. 728. 729. 730. 731. 732. 733. 734. 735. 736. 737. 738. 739. 740. 741. 742. 743. 744. 745. 746. 747. 748. 749. 750. 751. 752. 753. 754. 755. 756. 757. 758. 759. 760. 761. 762. 763. 764. 765. 766. 767. 768. 769. 770. 771. 772. 773. 774. 775. 776. 777. 778. 779. 780. 781. 782. 783. 784. 785. 786. 787. 788. 789. 790. 791. 792. 793. 794. 795. 796. 797. 798. 799. 800. 801. 802. 803. 804. 805. 806. 807. 808. 809. 810. 811. 812. 813. 814. 815. 816. 817. 818. 819. 820. 821. 822. 823. 824. 825. 826. 827. 828. 829. 830. 831. 832. 833. 834. 835. 836. 837. 838. 839. 840.

リル) - 1 - エチルピリジニウム - ジ・K. 2 - (p-ジメチルアミノ) - 3 - エチルベンザミド
ニウム - ジ・K. 2 - (p-ジメチルアミノ) - 3 - エチルベンザミド
ハブツク」(大河原 信、北尾徳次郎、平嶋 恒
高松照 警 鑑 議 診 社 1984年)に記録される

多くのフニ基を有する色素化合物を本発明に用いることができる。また、これらの増感色素はホログラムの使用目的によって異なる化学作用放射線の波長に合うように選択することができ、用途によっては2種類以上を組合わせて使用することも可能である。

【0028】次に本発明の成分(E)光あるいは熱などの外的作用によりスルホン酸誘導体を生成する化合物は、光あるいは熱などの外的作用によって、下記一般式(1)で表されるスルホン酸誘導体が生成するものであるといふ。

【化3】



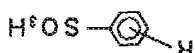
(1)

(式中、Rは水素原子、アルキル基、ハロゲン基、ニトロ基、ヒドロキシ基、シアノ基、アミノ基或いはアル

コキシ基からなる一つ以上の置換基で芳香環を置換してなることを示す。)

【0029】成分(E)の化合物としては、具体的にはジフェニルヨードニトリルオロキシレート、4-メトキシジフェニルヨードニトリルオロキシレート

1. 4-7월 (4-7월)에 3월
 2. 4-7월 (4-7월)에 3월
 3. 4-7월 (4-7월)에 3월
 4. 4-7월 (4-7월)에 3월
 5. 4-7월 (4-7월)에 3월
 6. 4-7월 (4-7월)에 3월
 7. 4-7월 (4-7월)에 3월
 8. 4-7월 (4-7월)에 3월
 9. 4-7월 (4-7월)에 3월
 10. 4-7월 (4-7월)에 3월
 11. 4-7월 (4-7월)에 3월
 12. 4-7월 (4-7월)에 3월



(1)

13

1957年

【0028】次に本発明の成分(E)光あるいは熱などの外的作用によりスルホン酸誘導体を生成する化合物は、光あるいは熱などの外的作用によって、下記一般式(1)で表されるスルホン酸誘導体が生成するものである。

亮、松岡 賢 編 講談社 1986年)に記載される多くのフニル基を有する色素化合物を本発明に用いることができる。また、これらの増感色素はホログラムの使用目的によって異なる化学作用放射線の波長に合うように選択することができ、用途によっては2種類以上を組

ナルビリニヨ一ジク、2-(p-ジナルブミノナル
リル)-1-エナルビリニナルヨ一ジク、2-(p-
ジナルブミノナルリル)-3-エナルベソナルブリ
ニナルヨ一ジクなどが挙げられる。その他には、「色素
ハズク」(大河原 信、北尾徳次郎、平嶋 恒

-ジク、3-エナル-2-(3-
シオキサリニツン)-1-
ノロハニル、
キサリニツムΔヨ-ジク。3-エナル-5-[2-(3
-エナル-2-ヘソリアリニツン)エチアソ]ロー
グニン、2-(p-ジメチルアミノメタシル)-1-エ

EVAU=UJAJA\N{VAX(VUJ/K-(H
I)Z-V-E-I)}-Z-V-E-E-JK-E
AU=UJAJA\N-H-E-{VAX(VUJ=UJAJA
JA\N-Z-V-E-I)-(E)-Z-V-E-E-JK
/KA\O-K-{VAX(VUJ=UJAJA

- (ジエナルミノ) -7エナル) x4レノ) -シクロ
 ルノノノ, 2, 5-エナル) (4- (ジナルミノ)
 -7エナル) x4レノ) -シクロノノノ, 2, 6-
 エナル) (4- (ジナルミノ) -7エナル) x4レ
 ノ) -シクロノノノ, 2, 6-エナル) (4- (ジナルミノ)

[illegible]

重合可能なエチレン性不飽和結合を少なくとも1個以上有し、かつ樹脂(A)と屈折率の異なる重合性モノマーと、(C)化学作用放射線に露光するとラジカル重合を活性化する光開始剤と、(D)光開始剤(C)を増感するフミノ基を有する増感色素と、(E)光あるいは熱などの外的作用によりスルホン酸誘導体を生成する化合物からなり、樹脂(A)及び重合性モノマー(B)の混合比は、樹脂(A)が過剰であるとして、(A)によるホログラフツク露光で重合するモノマー量が不足するために高い屈折率変動が得られないことや、また重合性モノマー(B)が過剰であると最初のホログラフツク露光で重合せずに系内に残留するモノマーが、製造工程において散乱しながら重合を起し、一旦形成されたホログラムの干渉縞が乱れ、高い屈折率変動が得られないことがあ

なおおるいホログラムを得るための樹脂 (A) 及び重合性モノマー (B) の組み合わせについては、例としては上記した米国特許第4942112号公報、米国特許第509803号公報、特開平2-3081号公報、特開平2-3082号公報、特開平5-107999、特開平5-94014号公報、或いは本出願人による特願平6-46742号、特願平6-149796号、特願平6-149797号、特願平6-149798号、特願平6-148244号、特願平6-148245号、特願平6-178812号等に記載されている。また成分 (C) の光開始剤の量は、成分 (A) 100重量部に対し、0.1から20重量部、好ましくは1から10重量部である。さらに、成分 (D) の増感色素は、成分 (A) 100重量部に対して0.1から10重量部、好ましくは0.5から5までの範囲をとることが可能である。

る。

【0032】このように、透明ホログラム用感光熱記録材料の各成分を適宜選択し、任意の割合で混合して得た感光液をスピンコート、ロールコート、バーコートなど公知の塗工手段を用いて、ガラス板やポリカーボネート板、ポリメチルメタクリレート板、ポリエスチルフィルムなどの基板2上に皮膜状に塗布したものが図1に示すホログラムが作製される通常のホログラム撮影用の透明ホログラム用感光性記録媒体1である。さらに感光層3上には酸素遮断膜として保護層4を設けてもよ

い。保護層４には例えば上記基板２と同等なもの、或いはポリオレフィン、ポリ塩化ビニル、ポリ塩化ビニリチン、ポリビニルアルコールまたはポリエチレンテレフタレートなどのプラスチック、ガラスなど光学的に透明なものを用いて、感光層を挟持する貼り合わせや押出機などによる積層、或いは溶液の塗工などにより形成される。なお、感光液を塗布する際は、必要に応じて適当な溶剤で希釈してもよいが、その場合には基板上に塗布した後に、乾燥を要する。

【００３３】さらに本発明の透明ホログラム用感光電致

[illegible]

駿)、DAM-201(みどり化学社製)、P1-10
 5(みどり化学社製)、ND1-105(みどり化学社
 製)、NAI-105(みどり化学社製)、ジフエニル
 ホネー、P-ニトロベンジル-9、10-ジエトキシ
 フトラセ-2-アルホネー、P-ニトロベンジル
 -9、10-ジエトキシフトラセ-2-アルホネー
 ト、ベンジルP-クロロベンゼンアルホネー、ベンジ
 ルm-クロロベンゼンアルホネー、ベンジルP-メ
 キシベンゼンアルホネー、ベンジルP-シアノベンゼ
 ンアルホネー、P-クロロベンジル、P-クロロベン
 ズアルホネー、m-クロロベンジルP-クロロベン
 ズアルホネー、p-エチルベンジルP-クロロベン
 ズアルホネー

[illegible]

【0030】なお、これらに限定されるものではなく、一般に相当するアルコールとポリアルケンポリクロライドやメチルアルコールなどのアルコール誘導体の酸塩化物との反応で得られるスルホン酸エステルを用いることもできる。これらは2種類以上を組み合わせて使用しても構わない。

【0031】本発明の透明ホログラム用感光記録材料は、上記したように(A)溶解性で、溶解可溶性で常溫、常圧で固体である樹脂と、(B)常溫、常圧で常溫、常圧で液体である樹脂と、(C)常溫、常圧で液体で、かつ常圧で沸点が100℃以上であるラジカル

短波長側にシフトし紫外長域に移るため、可視領域

(400〜700nm)での退色・消色が生じる。また

4級化したアミノ基を有する増感色素(D)は耐候性、

保存安定性に優れており、長期にわたる保存においても

分解などにより着色が起こらず、安定した透明なホログ

ラムが得られる。

【0038】以下、具体的な実施例により本発明をさら

に詳細に説明する。

<実施例1>ビスフェノールA型エポキシ樹脂(商品名

「エポコート1007」油化シエルフ社製)1

00重量部、トリエチレングリコールジブチレート5

0重量部およびジブチレニルエーテルニウムヘキサフル

オスフェート5重量部、3,3'-カルボニルビス

(7-ジエチルアミノ)クマリン1重量部、2-ニコロ

ベンジルトリエート5重量部を2-ブタノール200重量

部に混合溶解したものを感光液とした。この感光液を膜

厚約15μmになるようにガラス基板に塗布し感光層を

形成した後、感光層上をポリビニルアルコール(PV

A)膜で覆い、透明ホログラム用感光性記録媒体1を作

製した。

【0039】透明ホログラム用感光性記録媒体1を、図

2に示すホログラム撮影用の二光束光学系により光源と

してアルゴンレーザー(514.5nm、露光量20mJ

/cm²)を用いて露光しホログラム画像を作製した

後、100℃で30分加熱処理を行った。さらに2-ニ

トロペンジルトリエートを光分解するために高圧水銀灯

で100mJ/cm²の光照射を行なった。

【0040】得られたホログラムを可視光域(400〜

700nm)における平均透過率を測定したところ90

%を示した。さらにこのホログラムを150℃で1時間

加熱処理したところ、酸化等によるシートの着色が生じ

ることはなく、同様にシートの可視光域(400〜70

0nm)における平均透過率を測定したところ90%を

示した。なお、上記スルホン酸誘導体処理前の段階での

透過率は60%T前後である。また、そのホログラムの

回折効率、日本分光工業(株)製の分光光度計により

測定した。この分光光度計は、幅3mmのスリットを有

したフォトマルチplierを、試料を中心にした半径2

0cmの円周上に設置できるものである。測定条件は幅

0.3mmの単色光を試料に45度の角度で入射し、試

料からの回折光を検出した。正反射光以外で最も大きな

値と、試料を置かず直接入射光を受光したときの比

を回折効率とした。その結果は回折効率が95%であ

り、屈折率変動は0.0204であった。

【0041】<実施例2-5>実施例1の3-(2'-

ベンジルトリエート)-7-ジエチルアミノクマリン(D

ye-1)の代わりに3,3'-カルボニルビス(7-

ジエチルアミノクマリン)(Dye-2)、2,5-ビ

ス(4-(ジエチルアミノ)-7-エニル)メチレン

-シクロペンタノン(Dye-3)、2,6-ピカ

基が4級化されるため、増感色素(D)の吸収波長域が50

れるスルホン酸誘導体によって増感色素(D)のアミノ

する化合物(E)が光、熱などの外的作用により生成さ

感色素(D)は予め添加されるスルホン酸誘導体が発生

形成後の記録媒体中に残留することアミノ基を有する増

ラム画像記録が行われるものである。さらにホログラム

ら屈折率が異なることによる屈折率変動が生じ、ホログ

光干渉の強い部位と光干渉作用の弱い部位との密度差か

が低下するので、透明ホログラム用感光性記録媒体1の

では、ラジカル重合可能な重合性モノマー(B)の濃度

干渉の強い部位では、ラジカル重合可能な重合性モノマ

干渉の強い部位が生じる。このためレーザー照射部位の光

するため、その周囲のラジカル重合可能な重合性モノマ

せると光重合開始剤の作用によって、重合しポリマー化

(B)が、レーザー(レーザー光)照射により感光さ

有し、かつ成分(A)と屈折率の異なる重合性モノマー

重合可能なエチレン性不飽和結合を少なくとも1個以上

液体で、かつ常圧で沸点が100℃以上であるラジカル

である樹脂(A)中に均一に分散している常温、常圧で

干渉作用の強い部位は、溶媒可溶性で常温、常圧で固体

てレーザー照射を加えることにより、レーザー照射部位の光

ホログラム画像を記録する場合は、所望の画像に合わせ

【0037】この透明ホログラム用感光性記録媒体1に

定の酸などがある。

用としては、いわゆる外的刺激であり、光、熱以外の特

らの方法2種類以上組み合わせてもよい。なお、外的作

とがあるが、これに限定されるものではない。またこれ

面露光や、オーゾンやホットプレートなどによる加熱な

ク灯、超高圧水銀灯、メタルハライドランプ等による全

圧水銀灯、低圧水銀灯、キセノンランプ、カーボンアー

スルホン酸誘導体が発生させるための手段としては、高

【0036】さらにホログラム作製後に外的作用により

が、これに限定されるものではない。

リフトレーザー、ヘリウムネオンレーザー等が利用できる

は、ヘリウム-カドミウムレーザー、アルゴンレーザー、

の透明ホログラム用感光性記録材料に適した光源として

【0035】干渉パターン露光工程における、本発明

透過型ホログラムが得られる。

でも同様に可能であり、優れたホログラム特性を有する

説明及び図示をしないが透過型ホログラムの作製につい

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【0046】＜実施例1～5＞実施例1～5の2-ニトロベンジルシートの代わりにp-メトキシベンジルシートを用いる以外は、同様にホログラムを作製した。なお、2-ヒドロキシシートの代わりにp-メトキシベンジルシートを用いた場合は高圧水銀灯による光照射の代わりに130℃で10分間加熱処理を行ない、スルホン酸誘導体（p-トルエンスルホン酸）を生成させた。これも同様にホログラムの平均透過率、回折効率、屈折率変動を測定した。これを表★

★3に示す。ただし、T-1は、100℃で30分間加熱処理した後に130℃で10分間加熱処理を行った時の可視光域（400～700nm）におけるシートの平均透過率を測定したものであり、またT-2は、さらに150℃で1時間加熱した後の可視光域（400～700nm）におけるシートの平均透過率を測定したものである。【表3】

| 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.E.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|----------------|------------------------------|------------|-------------|-----------------|------------|------------|
| 実施例6
Dye-1 | 2.0 | 15.4 | 91 | 2.02 | 92 | 91 |
| 実施例7
Dye-2 | 2.0 | 15.1 | 94 | 2.24 | 92 | 92 |
| 実施例8
Dye-3 | 2.0 | 15.2 | 89 | 1.95 | 95 | 95 |
| 実施例9
Dye-4 | 2.0 | 16.3 | 96 | 2.32 | 90 | 88 |
| 実施例10
Dye-5 | 2.0 | 14.8 | 93 | 2.22 | 97 | 96 |

7「油化シエラエボキシ社製」の代わりに酢酸ビニル※

【0043】Dye-1: 3-(2'-ベンゾチアゾール)-7-ジエチルアミン/クワリツル
Dye-2: 3, 3'-カルボニルビス(7-ジエチルアミン/クワリツル)
Dye-3: 2, 5-ビス(4-ジエチルアミン/クワリツル)-シクロヘキサノン
Dye-4: 2, 6-ビス(4-ジメチルアミン/クワリツル)-シクロヘキサノン
Dye-5: 3-エチル-5-(2-(3-エチル-2-ベンゾチアゾリニリチン)エチリチン)ロータニン
【0044】＜実施例6～10＞実施例1～5のビスアノールA型エボキシ樹脂（商品名「エビコート10030」油化シエラエボキシ社製）の代わりに酢酸ビニル※を用い、さらにトリエチレングリコールジメタクリレート20の代わりにKAYARAD-R551（商品名日本化率社製）を用いる以外は、実施例1と同様にホログラムを作製し、平均透過率、回折効率、屈折率変動を測定した。その評価結果を表2に示す。ただし、T-1は、100℃で30分間加熱処理した後に高圧水銀灯で100mJ/cm²の光照射を行った時の可視光域（400～700nm）におけるシートの平均透過率を測定したものであり、またT-2は、さらに150℃で1時間加熱した後の可視光域（400～700nm）におけるシートの平均透過率を測定したものである。【表2】

| 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.E.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|---------------|------------------------------|------------|-------------|-----------------|------------|------------|
| 実施例1
Dye-1 | 2.0 | 16.8 | 94 | 2.04 | 90 | 90 |
| 実施例2
Dye-2 | 2.0 | 14.3 | 92 | 2.22 | 91 | 90 |
| 実施例3
Dye-3 | 2.0 | 15.4 | 94 | 2.22 | 95 | 94 |
| 実施例4
Dye-4 | 2.0 | 17.5 | 95 | 2.04 | 81 | 92 |
| 実施例5
Dye-5 | 2.0 | 15.7 | 97 | 2.54 | 97 | 96 |

域（400～700nm）におけるシートの平均透過率*

【0042】
*を測定したものであり、またT-2は、さらに150℃で1時間加熱した後の可視光域（400～700nm）におけるシートの平均透過率を測定したものである。なお、D、E、およびR、I、Cはそれぞれ回折効率、屈折率変動を示す。【表1】

| | 増感色素(D) | | | | | | T-2
(%) |
|-------|------------------------------|------------|-------------|-----------------|------------|------------|------------|
| | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.L.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) | |
| 実施例11 | Dye-1 | 2.0 | 19.0 | 9.4 | 1.87 | 9.0 | 9.1 |
| 実施例12 | Dye-2 | 2.0 | 14.5 | 9.1 | 2.06 | 9.1 | 9.2 |
| 実施例13 | Dye-3 | 2.0 | 18.1 | 9.6 | 2.07 | 9.3 | 9.2 |
| 実施例14 | Dye-4 | 2.0 | 16.8 | 9.4 | 2.03 | 9.4 | 9.4 |
| 実施例15 | Dye-5 | 2.0 | 15.6 | 9.3 | 2.09 | 9.6 | 9.6 |

【0048】＜実施例16～20＞実施例11～15の
p-メトキシベンジルトリオートの代わりには2-フェニ
ルエチルトリオートを用いる以外は、実施例11と同様
にホログラムを作製し、平均透過率、回折効率、屈折率
変動を測定した。その評価結果を表4に示す。ただし、
T-1は、100℃で30分間加熱処理した後130℃
で10分間加熱処理を行なった時の可視光域(400～*

【表4】

| | 増感色素(D) | | | | | | T-2
(%) |
|-------|------------------------------|------------|-------------|-----------------|------------|------------|------------|
| | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.L.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) | |
| 実施例16 | Dye-1 | 2.0 | 15.4 | 9.4 | 2.22 | 9.2 | 9.2 |
| 実施例17 | Dye-2 | 2.0 | 15.2 | 8.8 | 1.94 | 9.3 | 9.4 |
| 実施例18 | Dye-3 | 2.0 | 18.1 | 9.6 | 2.07 | 9.7 | 9.6 |
| 実施例19 | Dye-4 | 2.0 | 15.6 | 9.2 | 2.11 | 9.5 | 9.4 |
| 実施例20 | Dye-5 | 2.0 | 16.8 | 9.3 | 2.01 | 9.2 | 9.2 |

【0050】＜比較例1～5＞実施例1～5において、
2-ニトロベンジルトリオートを添加しないこと以外は
同様にホログラムを作製し、同様に平均透過率、回折効
率、屈折率変動を測定した。その評価結果を表5に示
す。ただし、T-1は、100℃で30分間加熱処理し
た後の可視光域(400～700nm)におけるシート
の平均透過率を測定したものであり、またT-2は、さ
らに150℃で1時間加熱した後の可視光域(400～
700nm)におけるシートの前平均透過率を測定したも※

【表5】

| | 増感色素(D) | | | | | | T-2
(%) |
|------|------------------------------|------------|-------------|-----------------|------------|------------|------------|
| | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.L.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) | |
| 比較例1 | Dye-1 | 2.0 | 16.5 | 8.8 | 2.28 | 6.3 | 5.5 |
| 比較例2 | Dye-2 | 2.0 | 16.3 | 8.6 | 2.43 | 5.9 | 5.2 |
| 比較例3 | Dye-3 | 2.0 | 15.6 | 9.2 | 2.07 | 7.0 | 6.4 |
| 比較例4 | Dye-4 | 2.0 | 15.5 | 8.9 | 2.11 | 5.5 | 5.1 |
| 比較例5 | Dye-5 | 2.0 | 13.1 | 8.8 | 2.20 | 6.2 | 5.7 |

【0052】＜比較例6～10＞実施例16～20にお
いて、2-フェニルエチルトリオートを添加しないこと
以外は同様にホログラムを作製し、同様に平均透過率、
回折効率、屈折率変動を測定した。その評価結果を表6
に示す。ただし、T-1は、100℃で30分間加熱処理※50
理した後の可視光域(400～700nm)におけるシ
ートの平均透過率を測定したものであり、またT-2
は、さらに150℃で1時間加熱した後の可視光域(4
00～700nm)におけるシートの前平均透過率を測定
したものである。これらは比較例1～5と同様に回折効

率、屈折率変調については光あるいは熱などの外的作用によりスルホン酸誘導体を生成する化合物である2-ニトロベンジルトリエーを添加しない場合でもほとんど変化は見られないが、透明性に大きな差を生じており、

【0053】

150℃に加熱処理した時点ではさらに低下した。

* 添加しない場合は光透過率が20〜30%低く、とくに

| | 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.E.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) |
|--------|---------|------------------------------|------------|-------------|-----------------|------------|------------|
| | | | | | | | |
| 比較例 6 | Dye-1 | 2.0 | 1.6, 8 | 9.4 | 2.03 | 6.3 | 5.4 |
| 比較例 7 | Dye-2 | 2.0 | 1.5, 4 | 9.1 | 2.01 | 6.2 | 5.4 |
| 比較例 8 | Dye-3 | 2.0 | 1.4, 7 | 9.3 | 2.23 | 6.9 | 6.1 |
| 比較例 9 | Dye-4 | 2.0 | 1.5, 7 | 9.2 | 2.10 | 5.7 | 5.1 |
| 比較例 10 | Dye-5 | 2.0 | 1.5, 3 | 8.5 | 2.25 | 6.1 | 5.5 |

【表6】

【0054】<比較例1>実施例1において、2-ニトロベンジルトリエーを添加しないこと以外は同様にホログラムを作製し、さらに実施例と同程度の退色が生じるように高圧水銀灯を用いて光照射を行なったところ、10J/cm²の光エネルギーを与えても可視光域(400〜700nm)におけるシートの平均透過率は80%程度にとどまった。

【0055】

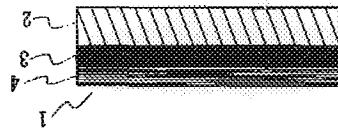
【図1】本発明の透明ホログラム用感光性記録材料からなる透明ホログラム用感光性記録媒体の構成を説明する概略図である。

【図2】ホログラム撮影用の二光束光学系を説明する概略図である。

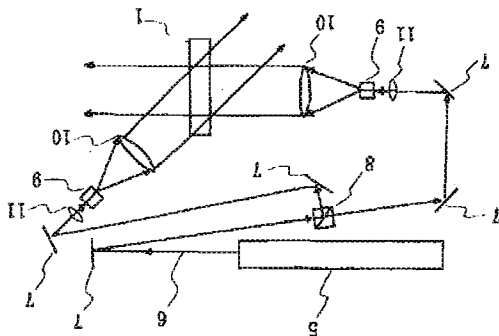
【符号の説明】

1 透明ホログラム用感光性記録媒体
2 基板
3 感光層
4 保護層
5 レーザ
6 レーザ光
7 ミラー
8 ビームスプリッター
9 スペリシアルフィルター
10 レンズ
11 レンズ

【図1】



【図2】



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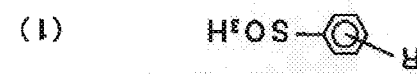
Notes:
1. Untranslatable words are replaced with asterisks (***).
2. Texts in the figures are not translated and shown as it is.

Translated: 04:19:26 JST 10/21/2011
Dictionary: Last updated 09/09/2011 / Priority: 1. Chemistry / 2. Electronic engineering / 3. Mathematics/Physics

CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1] A photosensitive recording material for transparent holograms which enters a reference beam which is chemical action radiation coherent in a recording medium characterized by comprising the following, and object light which is the same radiation, forms an interference pattern, and creates a hologram.
Resin which is essentially a solid in ordinary temperature and ordinary pressure at (A) solvent solubility.
(B) A polymerization nature monomer which has at least one or more ethylenic unsaturated bonds whose boiling points it is a fluid in ordinary temperature and ordinary pressure, and are not less than 100 °C in ordinary pressure, and in which a radical polymerization is possible and from which a component (A) and a refractive index differ.
(C) A photoinitiator which will activate a radical polymerization if it exposes in chemical action radiation.
(D) An amino group which carries out sensitization of the photoinitiator (C).

[Claim 2] The photosensitive recording material for transparent holograms according to claim 1, wherein a sulfonic acid derivative generated by external actions, such as light or heat, is denoted by a following general formula (1).



(Among a formula, R substitutes an aromatic ring by one or more functional groups which consist of a hydrogen atom, an alkyl group, a halogen group, a nitro group, hydroxyl, cyano groups, amino groups, or alkoxy groups, and things are shown.)
[Claim 3] A photosensitive recording medium for transparent holograms characterized by comprising the following.
A photosensitive layer which applies on a substrate and dries a sensitizing solution which dissolved in a solvent and prepared the photosensitive recording material for transparent holograms according to claim 1.
A protective layer.

[Claim 4] As opposed to a photosensitive layer of the photosensitive recording medium for transparent holograms according to claim 3, A manufacturing method of a transparent hologram which fades or decolorizes sensitizing dye which has said amino group with a sulfonic acid derivative generated from a compound which gives external actions, such as light or heat, and generates said sulfonic acid derivative after giving holographic exposure and forming a latent image, and is characterized by things.

[Detailed Description of the Invention]
[0001]

[Industrial Application] This invention is used for volume phase type hologram formation, and is exposed by high sensitivity to visible light, especially visible light, such as argon laser radiation. And hologram characteristic values, such as resolution, diffraction efficiency, and transparency, are good, and are related with the photosensitive recording material for transparent holograms which was further excellent in weatherability and preservation stability, the photosensitive recording medium for transparent holograms, and the manufacturing method of a transparent hologram using it.

[0002]

[Description of the Prior Art] Conventionally, since regeneration of a three-dimensional solid image is possible for a hologram, it is used for the display of covers, such as books and a magazine, POP, etc., the gift, etc. from the outstanding design nature and the ornament effect. Since it can say that a hologram is equivalent to record of the information on a submicron unit, it is used for the mark for forgery prevention, such as negotiable securities and a credit card, etc.

[0003] Since especially the volume phase type hologram can modulate a phase, without absorbing the light beam which passes an image by forming the spatial interference fringe from which the refractive index instead of optical absorbance differs into a hologram recording medium. In recent years, the application to the hologram optical element (HOE) represented by the head up display (HUD) for automobile loading other than a display use is expected.

[0004] By the way, a volume phase type hologram recording material is exposed by high sensitivity to a laser beam with a visible oscillation wavelength, and it is required that high definition should moreover be shown. In actually using it for formation of a hologram, it is required that characteristics, such as diffraction efficiency of a hologram, the wavelength reproducibility of regenerated light, and a band width (regenerated light full width at half maximum), should suit the purpose. When especially a head up display (HUD) etc. are used, importance is attached to having not only the above-mentioned hologram characteristics but higher transparency (light transmittance state). To excel in preservation stability over a long period of time is also needed.

[0005] The general principle about hologram production is written in some document and the technical books of Chapter 2, for example, a "holographic display" (the volume for Junpei Tsujiuchi; Sangyo Toshio Publishing). According to these, it is put on the coherent position of two luminous flux which irradiates a recording object thing with one side of a laser beam, and can generally receive the total reflection light from it, photosensitive recording medium, for example, dry plate for photographs. Another coherent light other than the reflected light from a subject is directly irradiated by the recording medium, without hitting a subject. Object light and the light directly

irradiated with the reflected light from a subject by the medium are called reference beam, and the interference fringe of a reference beam and object light is recorded as picture information. Next, if the processed recording medium is put to light and observed in the position of a suitable eye, the object image which the light from an illumination light source was diffracted by the hologram so that the wave face of the reflected light which reached the recording medium first from the subject on the occasion of record might be reproduced, and resembled the real image of the subject as a result will be observed in three dimensions. The hologram which enters a reference beam and object light in a recording medium from the same direction, and is formed is known as a transmission type hologram. Generally the hologram which was entered and was mutually formed from the opposite side of a recording medium on the other hand is known as a reflection type hologram. A transmission type hologram can be obtained by a publicly known method which is indicated, for example in the US,3506327,B gazette, the US,3894787,B gazette, etc. A reflection type hologram is producible by the publicly known method indicated by the US,3532406,B gazette, for example.

[0006] Reflective index modulation occurs as a value which compares the hologram formed as an image. This is a value of the incident light diffracted by the diffraction grating specified from diffraction efficiency and the thickness of a recording medium namely [comparatively], when the angle which two luminous flux makes with a medium directly similarly makes to a recording medium, and irradiates it and a diffraction grating is produced. Reflective index modulation is a quantitative measure of change of the refractive index produced in the exposure part of a volume type hologram and an unexposed part, i.e., the portion which light interferes and suits in slight strength, and the portion weakened mutually.

It can ask with the theoretical formula [Bell Syst. Tech. J., 48 and 2909, (1969)] of a KOGERU nick (H. Kogelnik).

Compared with a transmission type hologram, it is high-resolution, namely, generally, since a reflective phase type hologram has many interference fringes formed in per mm, it is difficult to record, and it is difficult to obtain high refractive index modulation.

[0007] There is the following as a recording material of such a volume phase type hologram. Conventionally, generally the sensitive material of a bleaching treatment silver salt and a dichromated gelatin system is used, and the sensitive material of this dichromated gelatin system is a material most widely used for recording a volume phase type hologram with those high diffraction efficiency and low noise characteristics. By the way, in order this sensitive material has a short shelf life, to have to prepare to the degree which is production and to perform wet developing. It is not a sensitive material which modification of a hologram is produced in swelling and the contraction process of gelatin which it is needed in the case of hologram production, and a silver salt sensitized material needs complicated treatment after record bad [the reproducibility of a hologram], and can be satisfied from a viewpoint of stability and workability. In addition, each of these above-mentioned sensitive materials has the problem of being inferior to an environmental capability-proof, for example, moisture resistance, and weatherability.

[0008] On the other hand, the hologram recording material using poly-N-vinylcarbazole as a material provided with the characteristics that it should excel in an environmental capability-proof, and should have hologram recording materials, such as high resolution and high diffraction efficiency, is raised. For example, the hologram recording material which consists of an annular ****-alpha-dicarbonyl compound and a sensitizer as a cross linking agent (JP, S60-45283, A). The hologram recording material which consists of 1,4,5,6,7,7-hexachloro-5-norbornene anhydrous-2,3-dicarboxylic acid and a pigment (JP, S60-227280, A). The hologram recording material (JP, S60-260080, A) which consists of 2,3-bornane dione and thioflavine, the hologram (JP, S62-123489, A) which consists of the thioflavine T and iodoform, etc. are proposed. However, since these hologram recording materials need wet developing too, since it is the sensitive material which needs a complicated treatment process, and has the problem of being inferior to reproducibility, and made poly-N-vinylcarbazole base resin, it is chemical stability, and although excelled in high resolution and an environmental capability-proof, it crystallizes, and is very easy to whiten poly-N-vinylcarbazole, and the reproducibility of transparency has the problem that it will be bad and a solvent will also be restricted. In addition, still much more improvement is desired in the sensitivity characteristic.

[0009] As a material which can carry out photo-curing by high sensitivity, it is a composition component of a photopolymerization initiator. The photo-curing resin composition used in the combination of 3-keto coumarin and diaryliodonium salt (JP, S60-88005, A). The hologram recording material (JP, H4-31590, A) which combined polymethylmethacrylate as this photopolymerization initiator and a support polymer is proposed. Although it is chemically stable and has high resolution and high sensitivity, in order to make an opening form by a wet process, Since **** polymer dissolves in a swelling solvent a little in expansion of dispersion in the peak wavelength of a reproducing wave length, or the half band width of peak wavelength, and the case of development. Since it has the problem that development nonuniformity occurs easily and many openings exist in a hologram further, it has the problem of being inferior to a heat-resisting property and heat-resistant

pressure nature.

[0010] Then, the photopolymerization type sensitive material which can produce a hologram is indicated by the US,3993485,B gazette and the US,3658526,B gazette at 1 time of a treatment process without a wet process. The former has a sensitive material of two types and, [as the 1st example] reactivity and a refractive index — things — the combination of the unsaturated ethylenic monomer and photopolymerization initiator in which two polymerizations are possible. For example, it is a photosensitive resin composition which can carry out hologram recording by

consisting of cyclohexyl methacrylate, N-vinylcarbazole, and benzoin methyl ether, sandwiching this in the glass plate of two sheets, and exposing by a 2 luminous-flux optical system. The unsaturated ethylenic monomer which has a comparable refractive index as the 2nd example and which can be polymerized and the unsaturated ethylenic monomer which works as a cross linking agent when it polymerizes. And four ingredients of two monomers, the nonresponsive compound which differs in a refractive index, and a polymerization initiator. For example, it is a photosensitive resin composition which consists of butyl methacrylate, ethylene glycol dimethacrylate, 1-phenylinaphthalene, and benzoin methyl ether, and can produce a hologram like the 1st example. Even if it uses which photosensitive resin composition, the polymerization of a reactant high monomer progresses more in the portion to which the light intensity of the interference fringe made according to two luminous flux becomes strong, and. The concentration gradient of a monomer arises and a reactant high monomer diffuses a reactant low monomer or nonresponsive compound into a portion with strong light intensity again at a portion with weak light intensity. Thus, an interference fringe is recorded with the difference of a refractive index, and a volume phase type hologram is formed.

[0011] [the latter US,3658526,B gazette] The manufacturing method of the stable hologram which consists of a hologram recording material which blended the fluid monomer, the ethylenic monomer in which photopolymerization is possible, and the photopolymerization initiator into the polymer matrix is indicated, and an eternal volume phase type hologram is obtained by 1-time exposure of chemical action radiation. The complete exposure of the continuing chemical action radiation is fixed to the hologram formed.

[0012] It is indicated by the US,4942112,B gazette, the US,5098803,B gazette, JP,H2-3081,A, and JP,H2-3082,A as improvement art also including the manufacturing method of the hologram recording material indicated by the US,3658526,B gazette. Thermoplastics, the unsaturated ethylenic monomer which can be polymerized, and a photopolymerization initiator are made into basic composition at these, in order to raise refractive index modulation, it is made to become refractive index difference at either thermoplastics or the unsaturated ethylenic monomer which can be polymerized using the compound which has an aromatic ring, [like that by which the US,3658526,B gazette indication is carried out] Since many light exposures are needed and high diffraction efficiency cannot be acquired from restriction of the diffusibility of the monomer at the time of exposure by using resin of the amount of polymers as binder MATORIKUSSU, the nonresponsive plasticizer has been added.

[0013] According to JP,H5-107999,A, what blended the cation pile affinity monomer and the cationic initiator instead of the plasticizer in the above-mentioned patent is proposed. The photosensitive resin composition for hologram recording which consists of an epoxy resin, a radical polymerization nature unsaturated ethylenic monomer, and an optical radical polymerization agent is indicated by JP,5-94014,A.

[0014]

[Problem to be solved by the invention] [the above-mentioned recording material of a volume phase type hologram] The problem etc. of the preservation stability by addition of the problem of the polymerization nature of the monomer for obtaining refractive index modulation, or dispersibility, the carrier which supports a monomer, and a nonresponsive additive, Although it furthermore has a problem of hologram characteristics, such as workability in hologram production, diffraction efficiency of the hologram obtained, transparency, and reproducibility, respectively,

[photopolymerization type sensitive material **** especially using a dry developing method] In order that the sensitizing dye used as problem common to all at the time of hologram formation may remain in a system as it is, there is a problem used as the colored hologram and it has been a serious problem in the use of optical elements, such as a head up display (HUD) in which high permeability is demanded especially. Then, while the hologram formation by dry processing is possible for this invention and being high transparency, it excels in weatherability. And it aims at providing the transparent hologram photosensitive recording material excellent in high resolution, high diffraction efficiency, and reproducing wave length reproducibility, a transparent hologram photosensitive recording medium, and the manufacturing method of a transparent hologram using it.

[0015]

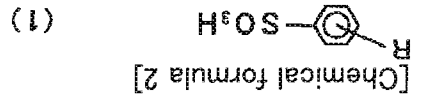
[Means for solving problem] the photosensitive recording material for transparent holograms, wherein this invention consists of sensitizing dye and a compound which generates a sulfonic acid derivative by external actions, such as (E) light or heat. [It is made that an aforementioned problem characterized by comprising the following should be solved, and, [the invention according to claim 1] The photosensitive recording material for transparent holograms which enters the reference beam which is coherent chemical action radiation, and the object light which is the same radiation into a recording medium, forms an interference pattern, and creates a hologram. Resin which is essentially a solid in ordinary temperature and ordinary pressure at (A) solvent solubility.

(B) The polymerization nature monomer which has at least one or more ethylenic unsaturated bonds whose boiling points it is a fluid in ordinary temperature and ordinary pressure, and are not less than 100 * in ordinary pressure, and in which a radical polymerization is possible and from which a component (A) and a refractive index differ.

(C) The photoinitiator which will activate a radical polymerization if it exposes in chemical action radiation.

(D) The amino group which carries out sensitization of the photoinitiator (C).

[0016] The compound in which the invention according to claim 2 generates a sulfonic acid derivative in the photosensitive recording material for transparent holograms of Claim 1 is denoted by a following general formula (1).



(Among a formula, R substitutes an aromatic ring by one or more substituents which consist of a hydrogen atom, an alkyl group, a halogen group, a nitro group, hydroxyl, cyano groups, amino groups, or alkoxy groups, and things are shown.)

[0017] It is a photosensitive recording medium for transparent holograms which the invention according to claim 3 provides the photosensitive layer which applies on a substrate and dries the sensitizing solution which dissolved in the solvent and prepared the photosensitive recording material for transparent holograms according to claim 1, and a protective layer, and is characterized by things.

[0018] The invention according to claim 4 receives the photosensitive layer of the photosensitive recording medium for transparent holograms according to claim 3. After giving holographic exposure and forming a latent image, external actions, such as light or heat, are given, it is a manufacturing method of the transparent hologram which fades or decolorizes the sensitizing dye which has said amino group with the sulfonic acid derivative generated from the compound which generates said sulfonic acid derivative, and is characterized by things.

[0019]

[Function] In this invention, although the aliphatic series monomer (B) in which a radical

polymerization is possible is uniformly distributed over resin (A) which is a solid in ordinary temperature and ordinary pressure by solvent solubility, it irradiates this recording material with laser interference light.

With therefore, the radical polymerization active species which the photoinitiator (D) produced from the photoinitiator (D) in the operation of sensitizing dye (C) in the strong part of the light interference operation in a laser radiation part, the concentration becomes high, and it becomes low in the weak part of the light interference operation in a laser radiation part. Resin (A) is extruded by the weak part of the light interference operation in a laser radiation part, the concentration in the portion becomes high, and the concentration in the strong part of the light interference operation in a laser radiation part falls. Thereby, since refractive index difference is produced in both parts, the latent image of a hologram is recorded.

[0020] and the thing for which external actions, such as light or heat, are given after hologram formation by adding the compound (E) which generates a sulfonic acid derivative by external actions such as light and heat. [The sensitizing dye (D) which has this amino group that remains in a

recording medium fades and decolorizes with a sulfonic acid derivative. [namely the sensitizing dye (D) currently added into the photosensitive recording material] Since the compound (E) which generates the sulfonic acid derivative added beforehand generates a sulfonic acid derivative by external actions, such as light and heat, and the amino group of sensitizing dye (D) is formed into 4 class by this, in order for the absorption wavelength region of sensitizing dye (D) to shift to the short wavelength side and to move to an ultra-violet wave length region, fading and the discharge in a visible region (400-700 nm) arise. The sensitizing dye (D) which has the amino group formed into 4 class is excellent in weatherability and preservation stability, in the preservation over a long period of time, coloring does not take place by decomposition etc., but the stable transparent hologram is obtained.

[0021][0021]. As for the feeling for transparent holograms of this invention, a recording material is ***** of refractive index modulation, diffraction efficiency, the peak wavelength of regenerated light, and its band width.

Application to the hologram optical element as which high transparency, such as a head up display, is required since it excels and the environmental capability—proof is also further excellent.

[0022]

[Working example] Hereafter, this invention is explained in detail. Drawing 1 is a schematic diagram explaining the composition of the photosensitive recording medium for transparent holograms which consists of a photosensitive recording material for transparent holograms of this invention, and drawing 2 is an approximate account figure explaining the 2 luminous-flux optical system for reflection type hologram photography.

[0023][the component (A) solvent solubility which constitutes the photosensitive recording material for transparent holograms of this invention] [as resin which is a solid in ordinary temperature and ordinary pressure] For example, polymethacrylic acid ester, polyacrylic acid, and those partial hydrolysates, Polyvinyl acetate, polystyrene, polyvinyl butyral, polyvinyl acetate, Polyvinyl formal, polyvinyl acetal, polychloroprene, Polyvinyl chloride, cellulose acetate, cellulose acetate butylate, Methyl cellulose, ethyl cellulose, chlorinated polyethylene, chlorinated polypropylene, Poly-N-vinylcarbazole, Poly N-vinyl pyrrolidone, vinyl polyacetic acid / acrylate, Vinyl polyacetic acid / methacrylate, ethylene/vinyl acetate copolymer, and styrene, Maleic anhydride, acrylic acid, methacrylic acid, acrylic acid ester, The thermoplastics represented by the copolymer etc. which consist of copolymerizable monomers, such as methacrylic acid ester, acrylamide, and methacrylamide, Bisphenol A and bisphenol B, bisphenol A F, the bisphenol S,

novolak, o-cresolnovolak, It is represented by the epoxy resin generated by the condensation reaction of various phenolic compounds, such as p-alkylphenol novolak, and epichlorohydrin, and a thermosetting resin is mentioned. Using also except above mentioned resin is possible, and it is not limited to these. By such solvent solubility, two or more kinds may be mixed and resin which is a solid in ordinary temperature and ordinary pressure may be used.

[0024] It has at least one or more ethylenic unsaturated bonds whose boiling points it is a fluid in component (B) ordinary temperature and ordinary pressure, and are not less than 100 °C in ordinary pressure and in which a radical polymerization is possible. And as a polymerization nature monomer from which a component (A) and a refractive index differ, at least one or more unsaturated bonds of ethylene nature may be included in a structural unit, a polyfunctional vinyl monomer other than the vinyl monomer which is one organic functions may be included, and they may be these mixtures. It is desirable for there to be 0.03 or more refractive index differences of a component (A) and a component (B) by the theory of a KOGERU nick (H. Kogelnik) mentioned above in fact.

[0025] Specifically Acrylic acid (meta), itaconic acid, maleic acid, acrylamide (meta), [high boiling point vinyl monomers, such as diacetone acrylamide and 2-hydroxyethyl (meta) acrylate, and a pan] An aliphatic series polyhydroxy compound, for example, ethylene glycol, diethylene glycol, triethylene glycol, a triethylene glycol, tetraethylene glycol, propylene glycol, Dipropylene glycol, tripropylene glycol, a tetrapropylene glycol, Neopentyl glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexandiol, 1,10-Decan diol, Trimethylolpropane, pentaerythritol, dipentaerythritol, 1,1 or poly(meta) acrylic ester, such as sorbitol and mannitol, Or allylic polyhydroxy compounds and aromatic polyhydroxy compounds, such as dimethylol tricyclodecane monoacrylate and dimethylol tricyclodecane diacrylate, For example, 1,1 or poly(meta) acrylic ester, such as hydroquinone, resorcinol, catechol, pyrogallol, and bisphenol A, The ethylene oxide denaturation (meta) acrylic ester of isocyanuric acid, 2-phenoxy ethyl methacrylate, phenol ethoxy rate monoacrylate, p-chlorophenyl acrylate, KAYARAD-R551 (made by trade name Nippon Kayaku Co., Ltd.), etc. are mentioned.

[0026] as a photoinitiator system which will activate a radical polymerization if it exposes in the component (C) chemical action radiation of this invention] Macromolecules, 10, a compound given in 1307(1977). For example, diphenyliodonium, ditolyl iodonium, phenyl (p-anisyl) iodonium, Bis(m-nitrophenyl)iodonium, bis(p-tert-butylphenyl)iodonium, Chloride of iodonium, such as bis(p-chlorophenyl)iodonium, Bromide or Howe fluoride salt, a hexafluorophosphate salt, Iodonium salt, such as a hexafluoroarsenate salt, a triarylsulfonium salt, Besides a triallyl phosphonium salt, an iron arene complex, etc., a tert-butyl peroxide iso-pig rate, 2,5-dimethyl-2,5-bis-(benzoyldioxy) hexane, 1,4-bis[alpha-(tert-butyl dioxy)-iso-propoxy] benzene, Di-tert-butyl peroxide, 2,5-dimethyl-2,5-bis-(tert-butyl dioxy)hexenehydroperoxide, alpha-(iso-propylphenyl)-iso-propylhydroperoxide, 2,5-bis-(hydroperoxy)-2,5-dimethylhexane, tert-butyl hydroperoxide, 1,1-bis(tert-butyl dioxy)-3,3,5-bird methylcyclohexanone, Butyl-4,4-bis(tert-butyl dioxy)valerate, cyclohexanone peroxide, 2,2',5,5'-tetra(tert-butylperoxy carbonyl) benzophenone, 3,3',4,4'-tetra(tert-butylperoxy carbonyl) benzophenone, 3,3',4,4'-tetra(tert-butylperoxy carbonyl) benzophenone, 3,3'-bis(tert-butylperoxy carbonyl)-4,4'-dicarboxy benzophenone, Organic peroxide, such as tert-butylperoxy benzoate and di-tert-butyl diperoxy isophthalate, Quinone, such as 9,10-ANSURA quinone, 1-chloroanthraquinone, 2-chloroanthraquinone, octa methylanthra quinone, and 1,2-benz ANSURA quinone, and benzoin methyl, benzoin ethyl ether, Benzoin derivatives, such as alpha-methylbenzoin and alpha-phenylbenzoin, etc. can be mentioned.

[0027] as component (D) sensitizing dye which has one or more kinds of amino groups which carry out sensitization of the photoinitiator (C) of this invention] Specifically Rhodamine B, Crystal Violet, malachite green, Auramine O, the phosphine R, an acridine orange, acridine yellow, Setoflavine T, brilliant Crais RUBURU, neutral red, CHIONIN, methylene blue, an indigo, PINASHI anol, tetraphenylporphyrin, A 3,3'-carbonyl screw (7'-diethylamino coumarin), 3-(2'-benzothiazole)-7-

(1) $\text{H}^{\text{e}}\text{OS}-\text{C}_6\text{H}_4-\text{H}$

or alkoxy groups, and things are shown.)

m-cyano benzyl tosylate, etc. can be mentioned.

[0030] The sulfonate obtained at the reaction of not the thing limited to these but an alcohol corresponding generally and acid chloride of sulfonic acid derivatives, such as p-tosyl chloride and methylsulfonyl chloride, can also be used. These may be used combining two or more kinds.

[0031] The sensitization thermal recording material for transparent holograms of this invention [As described above, by solvent solubility by (A) solvent solubility at resin which is a solid in ordinary temperature and ordinary pressure, and (B) ordinary temperature and ordinary pressure with a fluid, And the polymerization nature monomer where a boiling point has at least one or more ethylenic unsaturated bonds which are not less than 100 **, and in which a radical polymerization is possible by ordinary pressure and which differs in resin (A) and a refractive index, (C) The photoinitiator which will activate a radical polymerization if it exposes in chemical action radiation, (D) It consists of sensitizing dye which has an amino group which carries out sensitization of the photoinitiator (C), and a compound which generates a sulfonic acid derivative by external actions, such as (E) light or heat, [the mixing ratio of resin (A) and a polymerization nature monomer (B)] Since the monomer amounts in which resin (A) polymerizes in holographic exposure according being superfluous to a laser run short, high refractive index modulation is not obtained, [the monomer which remains in a system without a polymerization nature monomer (B) polymerizing that it is superfluous in the first holographic exposure] Since a polymerization is caused, the interference fringe of the once formed hologram is confused and high refractive index modulation may not be obtained, being spread in a manufacturing process, about the mixed rate, it needs to be careful. [combination / resin (A) for obtaining a bright hologram, and / of a polymerization nature monomer (B)] The US,4942112B

gazette, the US,5098803B gazette above-mentioned as an example, JP,H2-3081A, JP,H2-3082A, JP,5-107999A, JP,H5-94014A, Or it is indicated to Tokuganhei6-46742 by these people, Tokuganhei6-149796, Tokuganhei6-149797, Tokuganhei6-149798, Tokuganhei6-148244, Tokuganhei6-148245, Tokuganhei6-178812, etc. The quantity of the photoinitiator of a component (C) is 1 to 10 weight sections from 0.1 preferably 20 weight sections to component (A) 100 weight section. The sensitizing dye of a component (D) can take the ranges from 0.5 to 5 from 0.1 preferably 10 weight sections to component (A) 100 weight section.

[0032] Thus, each component of the sensitization thermal recording material for transparent holograms is chosen suitably. The sensitizing solution mixed and obtained at an arbitrary rate A spin coater, a roll coater, Using publicly known coating means, such as bar coater, a glass plate and a polycarbonate plate, It is the photosensitive recording medium 1 for transparent holograms for the usual hologram photography with which the hologram which was applied in the shape of a coat on the substrates 2, such as a polymethylmethacrylate board and polyester film, shows to drawing 1 is produced. Furthermore on the photosensitive layer 3, the protective layer 4 may be formed as an oxygen interception film. To the protective layer 4, for example, what is equivalent to the above-mentioned substrate 2 or polyolefine, it is formed of the coating etc. of the lamination by pasting, extruders, etc. which pinch a photosensitive layer using a transparent thing optically, such as plastics, such as polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, or polyethylene terephthalate, and glass, or a solution. When applying a sensitizing solution, it may dilute with a suitable solvent if needed, but desiccation is required after applying on a substrate in that case. [0033] Furthermore, various additives, such as publicly known thermal-polymerization inhibitor, a chain transfer agent, and an antioxidant, may be added to the sensitization thermal recording material for transparent holograms of this invention if needed.

[0034] Drawing 2 is a schematic diagram explaining the 2 luminous-flux optical system for reflection type hologram photography, and the laser beam 5 oscillated from the laser 5 is irradiated by the medium 1 for hologram recording via the mirror 7, the beam splitter 8, the spatial filter 9, and the lens 10. In this invention, dry processing (light irradiation and/or heat treatment) is performing the fixing process after the hologram photography by exposure. Although this invention does not carry out detailed explanation and illustration, it is possible similarly about production of a transmission type hologram, and the transmission type hologram which has outstanding hologram characteristics

[0035] Although a helium cadmium laser, argon laser, a krypton laser, helium neon laser, etc. can be used as a light source suitable for the photosensitive recording material for transparent holograms of this invention in the exposure process of an interference pattern, it is not limited to this. [0036] [as a means for furthermore generating a sulfonic acid derivative by an external action after hologram production] Although there are heating by full exposure, oven, a hot plate, etc. by high pressure mercury vapor lamp, low pressure mercury lamp, xenon lamp, carbon arc light, ultrahigh pressure mercury lamp, a halide lamp, etc., it is not limited to this. Two or more kinds of these methods may combine. As an external action, it is what is called an external stimulus, and there are an acid specific in addition to light and heat etc.

[0037] When recording a hologram image on this photosensitive recording medium 1 for transparent holograms, By adding laser radiation according to a desired picture, [the strong part of a light interference operation of a laser radiation part] By the ordinary temperature and ordinary pressure at solvent solubility in resin (A) which is a solid, with a fluid, And a boiling point has at least one or more ethylenic unsaturated bonds which are not less than 100 °C and in which a radical polymerization is possible by ordinary pressure, And if the polymerization nature monomer (B) from which a component (A) and a refractive index differ makes it expose by laser (laser interference light) exposure, in order that it may polymerize and it may polymerize according to an operation of a photopolymerization initiator, movement of the polymerization nature monomer (B) in which the radical polymerization of the laser circumference is possible arises. For this reason, [the strong part of the light interference of a laser radiation part] The concentration of the polymerization nature monomer (B) in which a radical polymerization is possible becomes high, and, [the weak part of a light interference operation] Since the concentration of the polymerization nature monomer (B) in which a radical polymerization is possible falls, the refractive index modulation by refractive indices differing arises from the density difference of the strong part of the light interference of the photosensitive recording medium 1 for transparent holograms, and the weak part of a light interference operation, and hologram image record is performed. The compound (E) which generates the sulfonic acid derivative added beforehand the sensitizing dye (D) which has this amino group that furthermore remains in the recording medium after hologram formation light, in order for the absorption wavelength region of sensitizing dye (D) to shift to the short wavelength side since the amino group of sensitizing dye (D) is formed into 4 class with the sulfonic acid derivative generated by external actions, such as heat, and to move to an ultra-violet wave length region, fading and the discharge in a visible region (400-700 nm) arise. The sensitizing dye (D) which has the amino group formed into 4 class is excellent in weatherability and preservation stability, in the preservation over a long period of time, coloring does not take place by decomposition etc., but the stable transparent hologram is obtained. [0038] Hereafter, a concrete working example explains this invention still in detail.

<Working example 1> bisphenol A type epoxy resin (made by trade name "Epicat 1007" oil recovery shell epoxy company) 100 weight section, Triethylene-glycol-diacylate 50 weight section and diphenyliodonium hexafluorophosphate 5 weight section, What carried out the mixture solution of 3,3'-carbonyl bis(7-dieethylamino)coumarin 1 weight section and the 2-nitrobenzyl tosylate 5 weight section to 2-butanone 200 weight section was used as the sensitizing solution. After having applied this sensitizing solution to the glass substrate so that it might become about 15 micrometers of thickness, and forming a photosensitive layer, the photosensitive layer top was covered by the polyvinyl alcohol (PVA) film, and the photosensitive recording medium 1 for transparent holograms was produced.

[0039] After exposing the photosensitive recording medium 1 for transparent holograms according to the 2 luminous-flux optical system for hologram photography shown in drawing 2, using argon laser (514.5 nm, light exposure 20mJ/cm²) as a light source and producing a hologram image, heat-treatment was performed at 100 °C for 30 minutes. In order to carry out the photolysis of the 2-

nitrobenzyl tosylate to a pan, the high pressure mercury vapor lamp performed light irradiation of 100 mJ/cm².

[0040]90% was shown when average permeability [in / for the obtained hologram / a light region (400-700 nm)] was measured. When this hologram was furthermore heat-treated at 150 ** for 1 hour, coloring of the sheet by oxidation etc. was not produced, and 90% was shown when the average permeability in the light region (400-700 nm) of a sheet was measured similarly. The permeability in the stage before the above-mentioned sulfonic acid derivative treatment is before and after 60%T. The diffraction efficiency of the hologram was measured with the spectrophotometer made from Jasco Industry. This spectrophotometer can install a photograph multimeter with a 3-mm-wide slit on the circumference with a radius [centering on a sample] of 20 cm. Measurement conditions entered the 0.3-mm-wide monochromatic light into the sample at the angle of 45 degrees, and detected the diffracted light from a sample. The ratio of the biggest value and the time of receiving direct incident light, without placing a sample was made into diffraction efficiency except regular reflection light. The result was 95% in diffraction efficiency, and refractive index modulation was 0.0204.

[0041]Instead of 3-(2'-benzothiazole)-7'-diethylamino coumarin (Dye-1) of the <working-example 2-5> working example 1, a 3,3'-carbonyl screw (7'-diethylamino coumarin) (Dye-2), 2,5-screw [[phenyl 4-(diethylamino)-]] methylene]-cyclopentanone (Dye-3), 2,6-screw [[phenyl 4-(dimethylamino)-]] methylene]-cyclohexanone (Dye-4), Except using 3-ethyl-5-[2-(3-ethyl-2-benzorear ZORINIRIDEN) ethylidene] rhodanine (Dye-5), it carried out like the working example 1 and the average permeability of the hologram in each time was measured. This is shown in Table 1 together with the result of the working example 1. However, T-1 measures the average permeability of the sheet in the light region (400-700 nm) after irradiating with light, and T-2 measures the average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour. D.E. and R.I.C shows diffraction efficiency and refractive index modulation, respectively.

[Table 1]

| | 増色色素(D) | 透光率
(%) | 膜厚
(μm) | D.E.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|-------|---------|------------|------------|-------------|-----------------|------------|------------|
| | | | | | | | |
| 実施例 1 | Dye-1 | 2.0 | 16.8 | 9.4 | 2.04 | 9.0 | 9.0 |
| 実施例 2 | Dye-2 | 2.0 | 14.3 | 9.2 | 2.22 | 9.1 | 9.0 |
| 実施例 3 | Dye-3 | 2.0 | 15.4 | 9.4 | 2.22 | 9.5 | 9.4 |
| 実施例 4 | Dye-4 | 2.0 | 17.5 | 9.5 | 2.04 | 9.1 | 9.2 |
| 実施例 5 | Dye-5 | 2.0 | 15.7 | 9.7 | 2.54 | 9.7 | 9.6 |

[0043]Dye-1:3-(2'-benzothiazole)-7'-diethylamino coumarin Dye-2:3,3'-carbonyl screw (7'-diethylamino coumarin)
Dye-3: 2,5-screw [[4-(Diethylamino)-phenyl] methylene]-cyclopentanone Dye-4:2,6-screw-[[phenyl/ 4-(dimethylamino)-/]] methylene] cyclohexanone Dye-5:3-ethyl-5-[2-(3-ethyl-2-benzorear ZORINIRIDEN) ethylidene] rhodanine [0044] Vinyl acetate is used instead of the bisphenol A type epoxy resin (made by a trade name "Epicat 1007" oil recovery shell epoxy company) of the <working-example 6-10> working examples 1-5, Except furthermore using KAYARAD-R551 (made by trade name Nippon Kayaku Co., Ltd.) instead of triethylene glycol diacrylate, the hologram was produced like the working example 1 and average permeability, diffraction efficiency, and refractive index modulation were measured. The evaluation result is shown in Table 2. However, T-1 measures the average permeability of the sheet in a light region (400-700 nm) when a high pressure mercury vapor lamp performs light irradiation of 100 mJ/cm² after heat-treating for 30 minutes at 100 **, T-

2 measures the average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour.

[0045]

[Table 2]

| | 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.E.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|--------|---------|------------------------------|------------|-------------|-----------------|------------|------------|
| | | | | | | | |
| 実施例 6 | Dye-1 | 2.0 | 15.4 | 9.1 | 2.02 | 9.2 | 9.1 |
| 実施例 7 | Dye-2 | 2.0 | 15.1 | 9.4 | 2.24 | 9.2 | 9.2 |
| 実施例 8 | Dye-3 | 2.0 | 15.2 | 8.8 | 1.95 | 9.5 | 9.5 |
| 実施例 9 | Dye-4 | 2.0 | 16.3 | 9.6 | 2.32 | 9.0 | 8.8 |
| 実施例 10 | Dye-5 | 2.0 | 14.8 | 9.3 | 2.22 | 9.7 | 9.6 |

[0046]Except using p-methoxybenzyl tosylate instead of 2-nitrobenzyl tosylate of the <working-example 11-15> working examples 1-5, the hologram was produced similarly. When p-methoxybenzyl tosylate was used instead of 2-hydroxy tosylate, heat-treatment was performed for 10 minutes at 130 ** instead of the light irradiation by a high pressure mercury vapor lamp, and the sulfonic acid derivative (p-toluenesulfonic acid) was made to generate. This measured the average permeability of -TO of a hologram, diffraction efficiency, and refractive index modulation similarly. This is shown in Table 3. However, T-1 measures the average permeability of the sheet in a light region (400-700 nm) when heat-treatment is performed for 10 minutes at 130 ** after heat-treating for 30 minutes at 100 **, T-2 measures the average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour.

[0047]

[Table 3]

| | 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.E.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|--------|---------|------------------------------|------------|-------------|-----------------|------------|------------|
| | | | | | | | |
| 実施例 11 | Dye-1 | 2.0 | 19.0 | 9.4 | 1.87 | 9.0 | 9.1 |
| 実施例 12 | Dye-2 | 2.0 | 14.5 | 9.1 | 2.06 | 9.1 | 9.2 |
| 実施例 13 | Dye-3 | 2.0 | 18.1 | 9.6 | 2.07 | 9.3 | 9.2 |
| 実施例 14 | Dye-4 | 2.0 | 16.8 | 9.4 | 2.03 | 9.4 | 9.4 |
| 実施例 15 | Dye-5 | 2.0 | 15.6 | 9.3 | 2.09 | 9.6 | 9.6 |

[0048]Except using 2-phenylethyl tosylate instead of p-methoxybenzyl tosylate of the <working-example 16-20> working examples 11-15, the hologram was produced like the working example 11 and average permeability, diffraction efficiency, and refractive index modulation were measured. The evaluation result is shown in Table 4. However, T-1 measures the average permeability of the sheet in a light region (400-700 nm) when heat-treatment is performed for 10 minutes at 130 ** after heat-treating for 30 minutes at 100 **, T-2 measures the average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour.

[0049]

[Table 4]

| 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.R.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) |
|---------|------------------------------|------------|-------------|-----------------|------------|------------|
| | | | | | | |
| 実施例16 | Dye-1 | 2.0 | 15.4 | 9.4 | 2.22 | 9.2 |
| 実施例17 | Dye-2 | 2.0 | 15.2 | 8.8 | 1.94 | 9.3 |
| 実施例18 | Dye-3 | 2.0 | 18.1 | 9.6 | 2.07 | 9.7 |
| 実施例19 | Dye-4 | 2.0 | 15.6 | 9.2 | 2.11 | 9.5 |
| 実施例20 | Dye-5 | 2.0 | 16.8 | 9.3 | 2.01 | 9.2 |

[0050]In the <comparative example 1-5> working examples 1-5, except not adding 2-nitrobenzyl tosylate, the hologram was produced similarly and average permeability, diffraction efficiency, and refractive index modulation were measured similarly. The evaluation result is shown in Table 5. However, T-1 measures the average permeability of the sheet in the light region (400-700 nm) after heat-treating for 30 minutes at 100 **, and [T-2] The average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour is measured. Even when these do not add 2-nitrobenzyl tosylate which is diffraction efficiency and a compound which generates a sulfonic acid derivative by external actions, such as light or heat, about refractive index modulation, change is hardly seen, but. The big difference was produced in transparency, when not adding, the light transmittance state was low 20 to 30%, and when heat-treated especially at 150 **, it fell further.

Table 5

| 増感色素(D) | 露光量
(mJ/cm ²) | 膜厚
(μm) | D.R.
(%) | R.L.C
(×100) | T-1
(%) | T-2
(%) |
|---------|------------------------------|------------|-------------|-----------------|------------|------------|
| | | | | | | |
| 比較例1 | Dye-1 | 2.0 | 16.5 | 9.6 | 2.28 | 6.3 |
| 比較例2 | Dye-2 | 2.0 | 16.3 | 9.6 | 2.43 | 5.9 |
| 比較例3 | Dye-3 | 2.0 | 15.8 | 9.2 | 2.07 | 7.0 |
| 比較例4 | Dye-4 | 2.0 | 15.5 | 9.3 | 2.11 | 5.5 |
| 比較例5 | Dye-5 | 2.0 | 13.1 | 8.9 | 2.20 | 6.2 |

[0052]In the <comparative example 6-10> working examples 16-20, except not adding 2-phenylethyl tosylate, the hologram was produced similarly and average permeability, diffraction efficiency, and refractive index modulation were measured similarly. The evaluation result is shown in Table 6. However, T-1 measures the average permeability of the sheet in the light region (400-700 nm) after heat-treating for 30 minutes at 100 **, and [T-2] The average permeability of the sheet in the light region (400-700 nm) after heating at 150 more ** for 1 hour is measured. Even when these do not add 2-nitrobenzyl tosylate which is diffraction efficiency and a compound which generates a sulfonic acid derivative by external actions, such as light or heat, about refractive index modulation like the comparative examples 1-5, change is hardly seen, but the big difference is produced in transparency. When not adding, the light transmittance state was low 20 to 30%, and when heat-treated especially at 150 **, it fell further.

Table 6

| 増感色素(D) | 露光量
(mj/cm ²) | 膜厚
(μm) | D.B.
(%) | R.I.C
(×100) | T-1
(%) | T-2
(%) |
|-----------------|------------------------------|------------|-------------|-----------------|------------|------------|
| 比較例 6
Dye-1 | 2.0 | 16.8 | 9.4 | 2.03 | 6.3 | 5.4 |
| 比較例 7
Dye-2 | 2.0 | 15.4 | 9.1 | 2.01 | 6.2 | 5.4 |
| 比較例 8
Dye-3 | 2.0 | 14.7 | 9.3 | 2.23 | 6.9 | 6.1 |
| 比較例 9
Dye-4 | 2.0 | 15.7 | 9.2 | 2.10 | 5.7 | 5.1 |
| 比較例 10
Dye-5 | 2.0 | 15.8 | 6.5 | 2.25 | 6.1 | 5.5 |

[0054]In the <comparative example 11> working example 1, a hologram is similarly produced except not adding 2-nitrobenzyl tosylate. When light irradiation was performed using the high pressure mercury vapor lamp so that fading still more nearly comparable as an working example might arise, even if it gave the light energy of 10 J/cm², the average permeability of the sheet in a light region (400-700 nm) was only about 80%.

[Effect of the Invention][Effect of the Invention]. with, this invention being a fluid and with (A) solvent solubility in resin which is a solid obtaining in this invention, and (B) ordinary temperature and ordinary pressure, [this invention] [ordinary temperature and ordinary pressure] And the polymerization nature monomer where a boiling point has at least one or more ethylenic unsaturated bonds which are not less than 100 **, and in which a radical polymerization is possible by ordinary pressure and which differs in a component (A) and a refractive index, (C) The photoinitiator which will activate a radical polymerization if it exposes in chemical action radiation, the sensitizing dye which has an amino group which carries out sensitization of the (D) photoinitiator (C), and the compound which generates a sulfonic acid derivative by external actions, such as (E) light or heat. therefore, **** — the hologram which was excellent in weatherability, such as a heat-resisting property, and was chemically stabilized while the high transparency in a light region was acquired by things especially in dry processing — *****.

It can use for photosensitive recording materials for transparent holograms for hologram optical elements (HOE) with very high demand performance, such as a head up display, especially.

[Translation done.]